

CLAIMS

1. A process for the preparation of urethane resins, which comprises the steps of

(1) reacting one or more compounds selected from a zircoaluminate compound and a compound (compound (a)) which has an organic group (I) carrying at least one group selected from primary amino, secondary amino, acryloyl, hydroxy, epoxy and mercapto groups in the group and has a hydrolyzable group selected from alkoxy, acetoxy and oxime groups directly bonded to 1 to 10 silicon or titanium atoms, with one or more organic compounds (compound (b)) which can produce a compound having a secondary amino or hydroxy group by reacting with the organic group (I) or zircoaluminate compound, simultaneously or sequentially, to produce a zircoaluminate reaction product or compound (product A) having less than 2 secondary amino or hydroxy groups in one molecule and having the hydrolyzable group directly bonded to 1 to 10 silicone or titanium atoms,

(2) reacting one or more compounds or products selected from a polyol compound (compound (c)), a polythiol compound (compound (c-1)) and a product C obtained in the following step (4), with one or more compounds selected from a polyisocyanate compound (compound (d)) and a polyisothiocyanate (compound (d-1)), to produce a (thio)urethane prepolymer (product B) containing terminal isocyanate and/or isothiocyanate groups in an amount of 4% by weight or below, and

(3) reacting the product A with the product B in proportions of at least 0.5 equivalent or more of the product A per free isocyanate and/or isothiocyanate group of the product B:

Step (4): a compound (compound (e)) having at least one group (II) selected from amino, acryloyl, epoxy and mercapto groups at the terminal of the molecule and having a number-average molecular weight of 100 to 25000 is reacted with a compound (compound (f)) which can produce a compound having a secondary amino or hydroxy group by reacting with the group (II), to produce a compound (product (c)) having 0.2 or more secondary amino or hydroxy groups at the terminal of the molecule and having a number-average molecular weight of 100 to 25000.

2. A process for the preparation of urethane resins in which said product B and, said product A, and one or more compounds selected from a compound (compound (g)) which has an organic group (III) carrying a primary amino, secondary amino, hydroxy and/or mercapto group in the group and has a hydrolyzable group selected from alkoxy, acetoxy and oxime groups directly bonded to 1 to 10 silicon or titanium atoms, a zircoaluminate compound and a compound (compound (h)) having an organic group reactive with an isocyanate or isothiocyanate group are reacted simultaneously or sequentially in proportions of at least 0.5 equivalent or more of the total amount of said product A and one or more compounds per free isocyanate and or isothiocyanate group of said product B.

3. The process for the preparation of urethane resins according to claim 1 or 2, wherein said compound (a) is a compound (compound (a-1)) in which said organic group (I) is a group having one primary amino group, and said compound (b) is an α , β -unsaturated carbonyl compound or α , β -unsaturated nitrile compound (compound (i)).

4. The process for the preparation of urethane resins according to claim 1 or 2, wherein said compound (a) is a compound (compound (a-2)) in which said organic group (I) is a group having 2 or more primary or secondary amino groups or at least one primary amino group and secondary amino group, and said compound (b) is said compound (i), a compound (compound (1)) having less than 2 isocyanate groups and/or isothiocyanate groups in the molecule obtained by reacting a compound (compound (j)) having 2 or more isocyanate groups and/or isothiocyanate groups with a compound (compound (k)) having 1 to 2 active hydrogen atoms reactive with an isocyanate or isothiocyanate group in the molecule, or a monoisocyanate compound or monoisothiocyanate compound (compound (m)).

5. The process for the preparation of urethane resins according to claim 4, wherein said compound (k) is a compound selected from a monoalcohol, monoprimary amine, monosecondary amine, monoamide compound, monomalonyl compound, monocarboxylic acid and monothiol.

6. The process for the preparation of urethane resins according to claim 1 or 2, wherein said compound (a) is a compound (compound (a-3)) in which said organic group (I) is a group having an acryloyl group, and said compound (b) is a monoprimary amine compound (compound (n)), or a compound (compound (o)) having 2 or more primary or secondary amino groups, or at least one primary amino group and secondary amino group.

7. The process for the preparation of urethane resins according to claim 1 or 2, wherein said silicon compound (a) is a compound (compound (a-4)) in which said organic group (I) is a group having an epoxy group, and said compound (b) is a compound (compound (p)) having 0.2 or more active hydrogen atoms.

8. The process for the preparation of urethane resins according to claim 1 or 2, wherein said compound (a) is a compound (compound (a-5)) in which said organic group (I) is a group having a mercapto group or a compound (compound (a-2)) in which said organic group (I) is a group having at least one epoxy group, a hydroxy group-containing acrylate, a hydroxy group-containing maleimide, a compound (compound (q)) having at least one allyl group and one hydroxy group, a compound (compound (r)) having at least one epoxy group and having a hydrolyzable group selected from alkoxy, acetoxy and oxime groups directly bonded to 1 to 10 silicon or titanium atoms, or a zircoaluminate compound.

9. The process for the preparation of urethane resins according to claim 1 or 2, wherein said compound (a) is a compound (compound (a-6)) in which said organic group (I) is a group having a hydroxy group, and said compound (b) is the said compound (1) or said compound (m).

10. A process for the preparation of urethane resins, which comprises the steps of

(1) reacting said compound (a-3) and said compound (n) or said compound (o), then, reacting one or more compounds selected from said compound (i), said compound (l) and said compound (m) simultaneously or sequentially or produce a compound (product D) having less than 2 secondary amino or hydroxy groups in one molecule and having the hydrolyzable group directly bonded to 1 to 10 silicon atoms, and

(2) reacting the product D with the product B in proportions of at least 0.5 equivalent or more of the product D per free isocyanate and/or isothiocyanate group of the product B.

11. A process for the preparation of urethane resins, which comprises the steps of

(1) reacting said compound (a-4) and said compound (p), then, reacting one or more compounds selected from said compound (i), said compound (l) and said compound (m) simultaneously or sequentially or produce a compound (product E) having less than 2 secondary amino or hydroxy groups in one molecule and having the hydrolyzable group directly bonded to 1 to 10 silicon atoms, and

(2) reacting the product E with the product B in proportions of at least 0.5 equivalent or more of the product E per free isocyanate and/or isothiocyanate group of the product B.

12. A process for the preparation of urethane resins which comprises the steps of

(1) reacting said compound (a-5) and/or said compound (a-2) and, said compound (q), said compound (r) or a zirconaluminate compound, then, reacting one or more compounds selected from said compound (i), said compound (l) and said compound (m) simultaneously or sequentially or produce a compound (product F) having less than 2 secondary amino or hydroxy groups in one molecule and having the hydrolyzable group directly bonded to 1 to 10 silicon atoms, and

(2) reacting the product F with the product B in proportions of at least 0.5 equivalent or more of the product F per free isocyanate and/or isothiocyanate group of the product B.

13. A process for the preparation of urethane resins in which a compound (compound (s)) having one hydroxy group and having a hydrolyzable group selected from alkoxy, acetoxy and oxime groups directly bonded to a silicon atom is reacted with the said product B in proportions of 1 equivalent or more of said compound (s) per free isocyanate and/or isothiocyanate group of said product B.

14. A process for the preparation of urethane resins, which comprises the steps of

(1) reacting said compound (t) having one or more hydroxy groups and/or more (meta)acryloyl groups with one or more compounds selected from said compound (l) and said compound (m) simultaneously or sequentially or produce a compound (product G) having less than 2 hydroxy groups in one molecule and having at least one (meta)acryloyl group, and

(2) reacting said product B with said product G or a compound (compound (t-1)) having one hydroxy group and at least one (meta)acryloyl group in an amount of 0.1 to 5 equivalent, or with said product G or said compound (t-1) in an amount of 0.1 to 5 equivalent and said product A in an amount of 0.2 equivalent or more per free isocyanate and/or isothiocyanate group of the product B.

15. A process for the preparation of urethane resins, which comprises the steps of

(1) reacting said compound (compound u) having over one hydroxy groups and one or more epoxy groups with one or more compounds selected from said compound (l) and said compound (m), simultaneously or sequentially or produce a compound (product H) having less than 2 hydroxy groups in one molecule and having at least one epoxy group, and

(2) reacting the product B with said product H or a compound (compound (u-1)) having one hydroxy group and at least one hydroxy group in an amount of 0.1 to 5 equivalent, or with said product H or said compound (u-1) in an amount of 0.1 to 5 equivalent and said product H in an amount of 0.9 equivalent or less per free isocyanate and/or isothiocyanate group of the product B, then reacting the product with said product A in an amount of less than 6 equivalent per epoxy group of said compound (u-1) or said product H.

16. A process for the preparation of urethane resins, which comprises the steps of

(1) reacting a compound (compound (v)) having 2 or more epoxy or acryloyl groups in the molecule with a zirconiumaluminate compound or a compound (compound (w)) which has an organic group (IV) carrying at least one group selected from primary amino, secondary amino and mercapto groups in the group and has a hydrolyzable group selected from alkoxy, acetoxy and oxime groups directly bonded to 1 to 10 silicon or titanium atoms in an amount of 0.5 to 2 equivalent based on said compound 9v), then reacting one or more compounds selected from said compound (i), said compound (I) and said compound (m) simultaneously or sequentially or produce a compound (product I) having less than 2 secondary amino or hydroxy groups in one molecule and having the hydrolyzable group directly bonded to 1 to 10 silicon or titanium atoms, and

(2) reacting the product I with the product B in proportions of at least 0.5 equivalent or more of said product I per free isocyanate and/or isothiocyanate group of said the product B.

17. A process for the preparation of urethane resins, which comprises the steps of

(1) reacting a compound (compound (x)) having over one groups reactive with a isocyanate and/or isothiocyanate group and at least one epoxy, (meta)acryloyl, vinyl or ethynylene group with one or more compounds selected from said compound (i), said compound (I) and said compound (m) simultaneously or sequentially to produce a compound (product J) having less than 2 hydroxy or amino groups in one molecule and having at least one epoxy, (meta)acryloyl, vinyl or ethynylene group, and

(2) reacting said product B with said product J or a compound (compound (x-1)) having one group reactive with an isocyanate and/or isothiocyanate group and at least one epoxy, (meta)acryloyl, vinyl, or ethynylene group in an amount of 0.1 to 5 equivalent, or with said product J or said compound (x-1) in an amount of 0.1 to 5 equivalent and said product A in an amount of 0.9 equivalent or less per free isocyanate and/or isothiocyanate group of the product B, then reacting the product with said product A in an amount of less than 6 equivalent based on said compound (x-1) or said product J to produce a reaction product (product K), and further curing the product K with a curing agent.

18. A process for the preparation of urethane resins, which comprises the steps of

(1) polymerizing a (meta)acryloyl group-containing monomer, a hydroxy group-containing (meta)acrylate and/or a silicon compound (compound (y)) having at least a (meta)acryloyl group and having a hydrolyzable group selected from alkoxy, acetoxy and oxime groups directly bonded to 1 to 10 silicon atoms in the presence of one or more compounds or products selected from said compound (c), said compound (c-1) and said product C to obtain a polymer (product I),

(2) reacting the product L with one or more compounds selected from said compound (d) and said compound (d-1) to produce a (thio)urethane prepolymer (product M) containing an isocyanate and/or isothiocyanate group on the terminal thereof in an amount of 4% by weight or less, and

(3) reacting one or more products or compounds selected from said product A, said product D, said product E, said product F, said product I, said product (a-1), said product(a-2), said product (g), said product (h), said product (k), said product (o), said product (p), said product (q), said product (s), said product (t), said product (t-1), said product (u), and said product (u-1) described in claims 1, 3, 4, 5, 6, 7, 8 or 9 with said product M simultaneously or sequentially in proportions of said one or more products or compounds of 0.5 equivalent or more per free isocyanate and/or isothiocyanate group of said product M.

19. A process for the preparation of urethane resins in which said product B or said product M is reacted with one or more products or compounds selected from said product D, said product E, said product F, said product I, said product (a-1), said product (a-2), said product (g), said product (h), said product (k), said product (o), said product (p), said product (q), said product (s), said product (t), said product (t-1), said product (u) and said product (u-1) simultaneously or sequentially in proportions of the total amount of said compound A and said one or more products or compounds of 0.5 equivalent or more per free isocyanate and/or isothiocyanate group of said product B or said product M.

20. A process for the preparation of urethane resins in which said product B or said product M is reacted with a zirconiumaluminate compound or a compound (compound (z)) which has an organic group carrying a mercapto group on the terminal in an amount of less than 1 equivalent per free isocyanate and/or isothiocyanate group of said product B or said product M and has a hydrolyzable group selected from alkoxy, acetoxy or oxime groups directly bonded to 1 to 10 silicon or titanium atoms, then, one or more products or compounds selected from said product A, said product D, said product E, said product F, said product I, said product (a-1), said product (a-2), said product (g) (excepting compounds having a mercapto group), said product (h) (excepting compounds having a mercapto group), said product (q), said product (s), said product (t), said product(t-1), said product (u) and said product (u-1) described in claims 1, 3, 4, 5, 6, 7, 8 or 9 and zirconiumaluminate compound are reacted in proportions of the total amount with said compound (z) or zirconiumaluminate compound of 0.5 equivalent or more per said isocyanate and/or isothiocyanate group.

21. A process for the preparation of urethane resins, which comprises the steps of

(1) reacting a zirconiumaluminate compound and a compound (compound (ab)) which has at least one active hydrogen atom reactive with an isocyanate or isothiocyanate group in the molecule and has a hydrolyzable group selected from alkoxy, acetoxy and oxime groups directly bonded to 1 to 10 silicon or titanium atoms with one or more compounds selected from said compound (1), said compound (m) and said compound (i) simultaneously or sequentially to produce a zirconiumaluminate reaction product or compound (product N) having less than 2 active hydrogen atoms reactive with an isocyanate or isothiocyanate group in the molecule and having the hydrolyzable group directly bonded to 1 to 10 silicon or titanium atoms,

(2) reacting the product N with said compound (j) or a compound (compound bb)) having 1.1. or more isocyanate or isothiocyanate groups in the molecule obtained by reacting said compound (j) with said compound (k) to produce a silicon compound (product o) having less than 2 isocyanate or isothiocyanate groups in the molecule and having the hydrolyzable group directly bonded to at least one silicon or titanium atom, and

(3) reacting the product o with one or more compounds or products selected from said compound (c), said compound (c-1), a compound (compound (cb)) having at least one primary amino or secondary amino group in the molecule, said product C and said product L.

22. The process for the preparation of urethane resins according to claims 21, wherein said compound (ab) is a compound carrying at least one group selected from primary amino, secondary amino, mercapto and hydroxy groups, and said compound (k) is a compound selected from monoalcohol, monoproprietary amine, monosecondary amine, monoalonyl compound, monocarboxylic acid, monothiol and monoamide compound.

23. A process for the preparation of urethane resins, which comprises the steps of

(1) reacting a compound (compound (db)) which has at least one active hydrogen atom reactive with an isocyanate or isothiocyanate group in the molecule and has at least one organic group (VII) selected from epoxy, (meta) acryloyl, vinyl and ethynylene groups with one or more compounds selected from said compound (1), said compound (m) and said compound(i) simultaneously or sequentially to produce a compound (product P) having less than 2 active hydrogen atoms reactive with an isocyanate or isothiocyanate group in the molecule and having at least one organic group (VII),

(2) reacting the product P with said compound (j) or said compound (bb) to produce a compound (product Q) having less than 2 isocyanate or isothiocyanate groups in the molecule and having at least one organic group(VII), and

(3) reacting the product Q with one or more compounds or products selected from said compound (c), said compound (c-1), said compound (cb), said product C and said product L.

24. The process for the preparation of urethane resins according to claims 23, wherein said compound (db) is a compound having at least one hydroxy group and at least one epoxy group.

25. The process for the preparation of urethane resins according to claims 23, wherein said compound (db) is a compound having at least one hydroxy or carboxyl group and at least one (meta) acryloyl group.

26. The process for the preparation of urethane resins according to claims 23, wherein said compound (db) is a compound having at least one group selected from primary amino, secondary amino, mercapto, hydroxy and carboxyl groups and having at least one vinyl or ethynylene group.

27. A process for the preparation of urethane resins, which comprises the steps of

(1) reacting a zircoaluminate compound or a silicon compound (compound (eb)) which has an organic (VIII) carrying at least one group selected from acryloyl, epoxy and mercapto groups in the group and has a hydrolyzable group selected from alkoxy, acetoxy and oxime groups directly bonded to at least one silicon atom with a compound (compound (fb)) which can produce a compound having a secondary amino or hydroxy group by reacting with the organic group (VIII), or after the reaction with said compound 9fb), reacting the product with one or more compound selected from said compound (1), said compound (m) and said compound (i) simultaneously or sequentially, to produce a zircoaluminate reacting product or silicon compound (product R) having less than 2 secondary amino or hydroxy groups in the molecule and having the hydrolyzable group directly bonded to at least one silicon atom

(2) reacting the product R with said compound (j) or said compound (bb) to produce a silicon compound (product S) having less than 2 isocyanate or isothiocyanate groups in the molecule and having at least one said hydrolyzable group directly bonded to a silicon atom, and

(3) reacting the product S with one or more compounds or products selected from said compound (c), said compound (c-1) said compound (cb), said product C and said product L.

28. The process for the preparation of urethane resins according to claim 26, wherein said compound (eb) is a group having at least one acryloyl group, and said compound (fb) is a compound having at least one group selected from primary and secondary groups.

29. The process for the preparation of urethane resins according to claim 27, wherein said compound (eb) is a compound in which said organic group (VIII) is composed of a group having at least one epoxy group, and said compound (fb) is a compound having an active hydrogen atom reactive with an epoxy group.

30. The process for the preparation of urethane resins according to claim 27, wherein said compound (eb) is a compound in which said organic group (VIII) is composed of a group having at least one mercapto group, and said compound (fb) is a compound having at least one epoxy group.

31. A process for the preparation of urethane resins, which comprises the steps of

(1) reacting a compound (compound (gb)) which has an organic group (IX) carrying at least one group selected from acryloyl, epoxy and mercapto groups (X) selected from epoxy (meta) acryloyl, vinyl and ethynylene groups with a compound (compound (hb)) which can produce a compound having a secondary amino or hydroxy group by reacting with the organic group (IX), or after the reaction with said compound (hb), reacting the product with one or more compound selected from said compound 91), said compound (m) and said compound (i) simultaneously or sequentially, to produce a compound (product T) having less than 2 secondary amino or hydroxy groups in the molecule and having at least one organic group (X),

(2) reacting to the product T with said compound (j) or said compound (bb) to produce a compound (product U) having less than 2 isocyanate groups in the molecule and having at least one said organic group (X), and

(3) reacting the product U with one or more compounds or products selected from said compound (c), said compound (c-1), said compound (cb), said product C and said product L.

32. The process for the preparation of urethane resins according to claim 31, wherein said compound (gb) is a compound in which said organic group (IX) is a compound composed of a group having 2 or more epoxy groups, and said compound (hb) is a monothiol compound or monosecondary amino compound.

33. The process for the preparation of urethane resins according to claim 31, wherein said compound (gb) is a compound in which said organic group (IX) is composed of a group having at least one acryloyl group and which has at least one (meta) acryloyl group, and said compound (hb) is a compound having one primary amino group.

34. The process for the preparation of urethane resins according to claim 31, wherein said compound (gb) is a compound in which said organic group (IX) is composed of a group having at least one epoxy group and which has at least one (meta) acryloyl group, and said compound (hb) is a compound having an active hydrogen atom reactive with an epoxy group.

35. The process for the preparation of urethane resins according to claim 31, wherein said compound (gb) is a compound in which said organic group (IX) is composed of a group having at least one acryloyl group and which has at least one vinyl group, and said compound (hb) is a compound having at least one primary amino group.

36. The process for the preparation of urethane resins according to claim 31, wherein said organic group (IX) is composed of a group having at least one mercapto group and which has at least one vinyl group, and said compound (hb) is a compound having an epoxy group.

37. A process for the preparation of urethane resins, which comprises the steps of

(1) reacting a zirconium compound or a compound (compound (ib)) which has one group (XI) selected from primary amino, secondary amino, hydroxy and mercapto groups in the group and has a hydrolyzable group selected from alkoxy, acetoxy and oxime groups directly bonded to at least one silicon or titanium atom with said compound (j) or said compound (bb) to produce a zirconium reaction product or compound (product V) having less than 2 isocyanate groups in the molecule and having the hydrolyzable group directly bonded to at least one silicon or titanium atom, and

(2) reacting the product V with one or more compounds or products selected from said compound (c), said compound (c-1), said compound (cb), said product C and said product L.

38. A process for the preparation of urethane resins, which comprises the steps of

(1) reacting a compound (compound (jb)) which has one group (XII) selected from primary amino, secondary amino, mercapto, hydroxy and carboxyl groups in the group and has at least one organic group (XIII) selected from epoxy, (meta) acryloyl, vinyl and ethynylene groups with said compound (j) or said compound (bb) to produce a compound (product W) having less than 2 isocyanate groups in the molecule and having at least one said organic group (XIII), and

(2) reacting the product W with one or more compounds or products selected from said compound (c), said compound (c-1), said compound (cb), said product C and said product L.

39. The process for the preparation of urethane resins according to claim 38, wherein said compound (jb) is a compound which has one hydroxy group and has at least one epoxy, (meta) acryloyl, vinyl or ethynylene group.

40. The process for the preparation of urethane resins according to claim 38, wherein said compound (jb) is a compound which has one group selected from primary amino, secondary amino, mercapto and carboxyl groups and has at least one vinyl or ethynylene group.

41. The process for the preparation of urethane resins according to any of claims 21 to 40, wherein said product O, said product Q, said product S, said product U, said product V or said product W (group 1) is reacted with one or more compounds or products (group 2) selected from said compound (c), said compound (cb), said product C and said product L, in an amount of the group 1 of 0.01 to 5 equivalent per hydroxy, mercapto, primary amino or secondary amino group of the group 2.

42. A process for the preparation of urethane resins in which a plurality of products (group 3) selected from said product O, said product Q, said product S, said product U, said product V and said product W are reacted with said group 2, in an amount of the group 3 of 0.01 to 5 equivalent per hydroxy, mercapto, primary amino or secondary amino group of the group 2.

43. The process for the preparation of urethane resins according to claim 42, wherein said group 3 is composed of combination of one or more products (group 4) selected from said product O, said product S and said product V with one or more products (group 5) selected from said product Q, said product U and said product W.

44. A process for the preparation of urethane resins, which comprises the step of reacting the urethane resin obtained by the process described in claim 23, 31 or 39 with a silicon compound having an organic group (XIV) reactive with an epoxy, acryloyl, vinyl or ethynylene group, a titanium compound or zircoaluminate compound having said organic group (XIV).

45. A process for the preparation of urethane resins, which comprises the step of reacting the urethane resin obtained by the process described in claim 23, 31 or 39 with a compound having an organic group reactive with an epoxy or acryloyl group and having at least one said organic group (X).